(12) UK Patent Application (19) GB (11) 2 029 837 A

(21) Application No **7837210**
(22) Date of filing **18 Sep 1978**
(23) Claims filed **18 Sep 1978**
(43) Application published **26 Mar 1980**
(51) **INT CL^3 C09K 3/28**
(52) Domestic classification **C3K** 120 123 201 210 272 283 291 EZ **C3W** 112 228 304
(56) Documents cited **None**
(58) Field of search **C3K**
(71) Applicant
Statni Vyzkumny Ustav Materialu, Praha, Czechoslovakia
(72) Inventors
Eduard Vasatko,
Vaclav Karasek,
Josef Kavalek
(74) Agent
Marks & Clerk

(54) **Fire-resistant Material**

(57) A fire-resistant material is formed from a binder which is preferably an unsaturated polyester or a polyepoxide, together with melamine, pentaerythritol, ammonium phosphate, a starch or dextrin, and an orthosilicic acid gel. These components are thoroughly mixed and an initiator or hardener is then added. The composition is suitable for making glass-reinforced laminates or coating structural steel members.

SPECIFICATION
Fire-resistant Material

The present invention relates to a composition which can be used to produce a fire-resistant material. Such material is also resistant to radiant heat, electrical discharges, mechanical damage, atmospheric exposure and to many organic solvents. The material is particularly useful for coating inflammable materials such as plastics, wood and cellular materials.

Several, reasonably effective methods are known of protecting inflammable materials against fire. Most known fire-proof coatings provide a protective or formable layer. Although such coatings have certain advantages, they have poor resistance to, for example, atmospheric exposure, water, and mechanical damage. Also, most of such coatings do not adhere sufficiently to a substrate after they have been foamed; as a result, they become inefficient after a short time. This is true of most coatings based on silicates or on organic salts.

Certain types of surface treated, coated or toughened compositions have excellent fire resistance. For example, in some countries, and recently in Czechoslovakia, protective foamable films have been made based on silicates or organic salts. These films are reinforced with glass or metal filaments and then superficially protected or finished with metallic or thermoplastic foils. However, such films or boards have many drawbacks of which the most troublesome is the difficulty of attaching the films to the materials to be protected, further the claims laid upon the superficial finish. Furthermore, the treated surface has poor resistance to mechanical damage. Such coatings are therefore only suitable for indoor applications since they have no long-term resistance to moisture or atmospheric exposure.

Some materials, especially plastics materials, may be treated with a fire-retardant. Such retardant may react with the material to which it is added, or it may simply be an additive. For example, hexachloroendomethylene-tetrahydrophthalic a anhydride has been added for many years to polyester resins to reduce inflammability. Also, tetrabromoxylene has been added to polymeric materials, for example polystyrene. It is also known to use a combination of a wide range of fire-retardant additives. Unfortunately, the addition of such additives can impair the physico-mechanical properties of the material to be treated, and perfect self-extinction and incombustibility are not always achieved. Furthermore, such additives are often rather expensive.

We have now discovered a method of fire-proofing an article which can overcome many of the drawbacks of known methods.

The present invention consists in a composition formed from: a binder; melamine; pentaerythritol; ammonium phosphate; dextrin and/or starch; and an orthosilicic acid gel. We prefer that for every 100 parts by weight of binder there are present from 5 to 30 parts of melamine, from 5 to 30 parts of pentaerythritol, from 8 to 35 parts of ammonium phosphate, from 3 to 25 parts of dextrin and/or starch, and 5 or less parts of orthosilicic acid gel.

The binder may be any suitable resin, but we prefer a polyester or a polyepoxide. Suitable polyester resins include ortho-, iso- and terephthalic acid type resins and bisphenol (preferably bisphenol A) type resins. Other types of polyester resins that may be used include epoxy polyesters and polyester resins based on vinyl esters.

The composition of the invention may be strenghened by mixing with it reinforcing fibres, such as E-type glass fibres, C-type glass fibres, mineral fibres (for example asbestos fibres), or fibres of superficially finished thermoplastic material. Such fibres may simply be mixed with composition, or they may be present in layers within the composition. In this second case it is more convenient to apply the composition to a preformed fibrous layer, which may be oriented or non-oriented and woven or non-woven.

The invention also consists in a method of producing a fire-resistant material which comprises adding an initiator to a homogenised composition of the invention. A reinforced fire-resistant material can be produced by applying the initiated composition to a reinforcing fibrous layer. The reinforcing fibrous layer may comprise E-type glass fibres, C-type glass fibres, or fibres of superficially finished thermoplastic material, and it preferably weighs from 10 to 900 grams per square metre.

Sheets or blocks of fire-resistant material may be preformed and used when they have set hard, or, alternatively, a homogeneous composition of the invention together with an initiator may be applied to an article to be protected and the composition allowed to harden.

The fire-resistant material of the invention may be made simply by homogenising the composition of the invention in any suitable homogeniser, preferably in an attrition roller or plate mill. After thorough homogenisation and just before further processing, one or more initiators are added to the composition. The composition is then applied to the article to be fire-proofed, or to a suitably shaped substrate if a sheet of fire-resistant material is desired. This can be done using a brush, roller or doctor blade, or by a mechanical method, such as screen or curtain coating, sprinkling, spreading, pouring, spraying or doctoring by a cylinder blade. The article or substrate should be degreased before the composition is applied. It is important that the composition is perfectly homogeneous before the initiator is added. If this is not the case some of the components of the composition may decompose. Any suitable polymerisation initiator may be used, and these are generally strong oxidising agents or highly alkaline compounds.

The composition can be applied to the article

or substrate to whatever thickness is necessary to give the desired fireproofing. The composition may be applied as one layer or, alternatively, a series of layers may be applied, each subsequent layer being added when its preceding layer has set. Where the composition is applied in thick layers it is sometimes preferable to reinforce such layers with one or more reinforcing fibrous layers. Reinforcing may be carried out manually (sometimes referred to as the contact manner), by means of a brush, doctor blade or roller, or by a mechanical method suitable for the manufacture of polyester glass-reinforced plastics, such as machine spraying, precise winding, cold pressing and centrifugal casting.

The composition will set more quickly if it is thermally cured at a temperature preferably not exceeding 80°C. It higher temperatures are used the composition may be prematurely decomposed.

The fire-resistant material of the invention is especially useful for reducing the inflammability of polymeric materials and wood. When the material is heated above 100—120°C it begins to soften, and foaming occurs when the tèmperature is from 150—180°C. The foamed material, which often has a thickness of from 8 to 10 mm, is a very good heat insulator and is able to prevent an easily inflammable material from flashing, catching fire or burning through. Such a layer of fire-resistant material is very compact and adheres well to many surfaces. For example, a polyester glass-reinforced laminate (which is especially suitable for treatment by the composition of the invention) coated with a 0.6 mm thick gel-coat containing the same binder as that used in the substrate did not catch fire when the surface was heated by a 1100°C propane-butane flame for more than 20—30 minutes. Even when the material is heated for longer periods, it burns locally but it does not completely catch fire. If the laminate is manufactured entirely from the modified binder of the invention combustion is completely prevented.

One advantage of the method of the invention is that the fire-resistant layer can be firmly attached to the article to be protected. This is especially true if the fire-resistant material and the article are composed of similar materials. It is also an advantage that the fire-resistant material can be produced cheaply using similar techniques to those already known. Furthermore, it is not necessary to use highly expensive modified polyester or epoxide resins, such as those based upon hexachloroendomethylenetetrahydrophthalic acid or other reactive retardants. The addition of the fire-resistant protective layer or gel-coat of the invention to both sides of a polyester or epoxide glass-reinforced laminate ensures excellent physico-mechanical properties. This is because the structure and function of the layer is substantially unaffected by the presence of the fire-resistant layer or by the subsequent heating and foaming treatment.

The fire-resistant material of the invention also affords an article excellent resistance to atmospheric exposure and to water. Such resistance can be enhanced by combining this material with a thin chemically resistant resinous gel-coat. An article treated in this way will be able to withstand many corrosive environments.

The invention is also useful for protecting other material such as wood and wooden structures. One or more layers applied to wood will protect the wood not only against fire but also against atmospheric exposure, mildew and ligniperdous fungi. The treatment also prevents wood from moistening or drying out, thereby extending the lifetime of the wood.

The fire-resistant material of the invention has a further advantage in that the binder may be wholly or partly combined with paints or varnished, especially those based on polyesters, epoxides or polyurethanes. In this way an excellent finish can be achieved, even when conventional techniques are used.

The material of the invention can also be used to coat steel structures, in which case the coating also serves to prevent corrosion.

The relative amounts of the components of the composition of the invention may vary widely. The precise amounts used will depend upon the type of binder and initiator, as well as on the chemical and atmospheric conditions and the type of material to be protected. In practice, however, it is a simple matter to determine optimum relative amounts, and the following examples, which further illustrate the present invention, give an indication in this respect.

Example 1

A fire-resistant gel-coating was applied to each side of an orthophthalic type polyester glass-reinforced laminate. The gel-coating was produced from the following components:

100 parts by weight of an orthophthalic type polyester resin;
16 parts by weight of melamine;
14 parts by weight of pentaerythritol;
8 parts by weight of potato starch; and
20 parts by weight of ammonium phosphate.

The components were thoroughly homogenised together with 1.5% of an sub-microscopic pyrogenic silica additive. After homogenisation, 3 parts by weight of methylcyclohexanone peroxide and about 1—1.5 parts by weight of cobalt naphthenate were added and the mixture was stirred. The stirred mixture was then applied by brush to a laminate mould of about 0.6 mm thickness. After the composition had partially polymerised it was possible to continue lamination by this contact process using an unmodified orthophthalic acid without a binder. This was continued until the desired laminate thickness had been achieved. The product was cut to the desired size and then coated with a 0.6 mm thick protective layer

having the composition given above. The product was then allowed to polymerise fully.

Example 2

A fire-resistant door panel was produced by coating a polyester glass-reinforced laminate. To achieve the degree of fire-resistance required by Czechoslovak standard No. 73085260 over a period of some 60 to 90 minutes it was found to be necessary to manufacture the complete door panel as one laminate. To prepare the coating the following components were mixed:

100 parts by weight of an isophthalic type polyester resin;
26 parts by weight of melamine;
20 parts by weight of pentaerythritol;
14 parts by weight of dextrin;
35 parts by weight of ammonium phosphate; and
0.5 parts by weight of silica.

This composition was homogenised and initiated by the addition of 3 parts by weight of methylethylketone peroxide and 1.5 parts by weight of cobalt naphthenate. A laminate was then manufactured using a conventional lamination technique.

Example 3

Here a fire-resistant layer was produced suitable for protection of a wooden gable. The fire-resistant material was treated by the addition of a paint to give a suitable surface finish. Firstly, 100 parts by weight of a bisphenolic type polyester resin and 5 parts by weight of a pigment paste suitable for polyesters were mixed. To this mixture were added the following:

10 parts by weight of melamine;
8 parts by weight of pentaerythritol;
11 parts by weight of ammonium phosphate;
4 parts by weight of starch; and
2.5 parts by weight of silica.

This mixture was homogenised and 3% by weight of benzoyl peroxide (based on the weight of binder) and 1.5 parts by weight of a 10% solution of dimethylaniline in styrene were added. The resulting coating composition may be thermally cured, for example by infrared radiation.

Example 4

A fire-resistant material was produced suitable for protecting steel girders. The following components were mixed:

100 parts by weight of an epoxide resin;
5 parts by weight of a pigment powder;
18 parts by weight of melamine;
16 parts by weight of pentaerythritol;
5 parts by weight of starch;
20 parts by weight of ammonium phosphate; and
5 parts by weight of silica.

This mixture was homogenised and 10 parts by weight of a cycloaliphatic polyamine hardener were added. The resulting coating mixture was then applied to the girders immediately.

Example 5

A polyester glass-reinforced laminate having excellent fire-resistance and excellent resistance to aggressive water was made in the following way. A gel-coat of a chemically resistant vinyl ester type resin was applied using a Polyspray spraying a device to a suitable substrate. To this gel coat was laminated by a contact process one layer of a glass reinforcement. This glass reinforcement weighed 135 grams per square metre and was formed from the following components:

100 parts by weight of an isophthalic type polyester resin;
16 parts by weight of melamine;
17 parts by weight of pentaerythritol;
5 parts by weight of starch;
17 parts by weight of ammonium phosphate;
3% by weight (based on the weight of binder) of methylethylketone peroxide; and
1% by weight (based on the weight of binder) of cobalt naphthenate.

The first five of these components were homogenized and then the peroxide and the naphthenate were added. When this protective layer had partially polymerised lamination was continued using a conventional machine spraying technique. A final surface layer of the same composition was then applied. In general, it will not be necessary to protect with a vinyl ester gel-coat both sides of structures such as roofs, eaves and gutters, since these are exposed to the weather from only one side.

Claims

1. A composition formed from; a binder; melamine; penetaerythritol; ammonium phosphate; dextrin and/or starch; and an orthosilicic acid gel.

2. A composition according to claim 1, which comprises 100 parts by weight of binder; from 5 to 30 parts by weight of melamine; from 5 to 30 parts by weight of pentaerythritol; from 8 to 35 parts by weight of ammonium phosphate; from 3 to 25 parts by weight of dextrin and/or starch; and 5 or less parts by weight of orthosilicic acid gel.

3. A composition according to claim 1 or claim 2, in which the binder comprises a polyester or a polyepoxide.

4. A composition according to claim 3, in which the polyester is formed from ortho, iso- or terephthalic acid as acid component.

5. A composition according to clain 3 or claim 4, in which the polyester is formed from a bisphenol as alcohol component.

6. A composition according to claim 3, in which the polyester is based on a vinyl ester.

7. A composition according to claim 3, in which the binder is an epoxy polyester.

8. A composition according to any one of the preceding claims, additionally comprising reinforcing fibres.

9. A composition according to claim 8, in which the fibres are E-type glass fibres, C-type glass fibres, mineral fibres, or fibres of superficially finished thermoplastic material.

10. A composition according to claim 9, in which the mineral fibres are asbestos fibres.

11. A composition according to claim 1, substantially as herein described with reference to any of the foregoing Examples.

12. A method of producing a fireresistant material, which comprises adding an initiator to a homogeneous composition according to any one of the preceding claims.

13. A method according to claim 12, which additionally comprises applying the initiated composition to a reinforcing fibrous layer.

14. A method according to claim 13, in which the fibrous layer comprises E-type glass fibres, C-type glass fibres, mineral fibres, or fibres of superficially finished thermoplastic material.

15. A method according to claim 14, in which the mineral fibres of the fibrous layer are asbestos fibres.

16. A method according to any one of claims 13 to 15, in which the fibrous layer weighs from 10 to 900 grams per square metre.

17. A method according to claim 12, substantially as herein described with reference to any one of the foregoing Examples.

18. A fire-resistant material when produced by a process according to any one of claims 12 to 17.

19. A process for fire-proofing an article which comprises applying to the surface of the article a homogeneous composition according to any one of claims 1 to 11 together with an initiator.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1980. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.